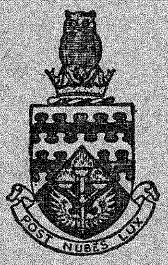


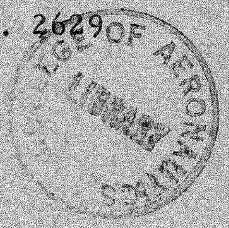
THE COLLEGE OF AERONAUTICS
CRANFIELD

CHARACTERISTICS OF THE HIGH TEMPERATURE MECHANISMS OF CREEP AND RECOVERY IN GRAPHITE

Contract No. D.A. - 91 - 591 - E.U.C. 2629

Final Technical Sheet No. 1

August 1st 1962 - July 31st 1963



CoA NOTE MAT. 1.

August, 1963

CRANFIELD

DEPARTMENT OF MATERIALS

Characteristics of the High Temperature Mechanisms of Creep and Recovery in Graphite

Contract No. D.A. - 91 - 591 - E.U.C. 2629

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The College of Aeronautics,
Cranfield, Bletchley,
Buckinghamshire, England.

ABSTRACT

An apparatus has been developed for determining the high temperature creep and recovery characteristics of graphite by applying torsional stresses to thin-walled tubes. This method has the advantages of a simple stress system, constant stress for constant load, easy rapid removal of load and the independence of the strain measurement from thermal expansion. Torsional stress-strain curves show a decreasing modulus with increasing temperature from 2000 - 2850°C. The rate of creep in this range is increased by increasing temperature and stress. Recovery rate is not so sensitive to increasing temperature. Using a method developed for metals, where recovery can be subtracted from forward creep, a secondary creep rate is deduced. This rate, when plotted according to the Arrhenius' equation, yields an activation energy for secondary creep of 154 kcals over the temperature range 2100 - 2700°C. These results are critically examined and the future extension of the work discussed.

Contents

List of figures

A. Summary and analysis of work performed.

This work is a continuation of that reported in F.T.R.I. of Contract No. DA-91-591-EUC-1759 dated 30th June, 1962. The torsional creep apparatus described in that report has been completed and calibrated. Some minor modifications suggested by experience with the apparatus have been incorporated and are described below.

The results on one commercial graphite (Morganite Carbon Ltd., E.Y.9) have been analysed and their significance is discussed.

1. Torsional creep apparatus

This apparatus was fully described in our previous report (1), and has only been slightly modified. These minor modifications, together with the calibration and loading techniques, are described below. A general view of the equipment is shown in Figure 1.

1.1 Test specimen

The torsional stressing of thin-walled tubes has certain advantages over conventional tensile, compression, and bending techniques. These are:-

a) For a constant load, the stress remains constant throughout the duration of the test.

b) If the wall thickness is small compared with the tube diameter, then the shear stress across its section may be regarded as uniform.

c) The measurement of strain is unaffected by thermal expansion and contraction.

d) It is comparatively easy to reverse the stress direction.

The dimensions of the test specimens are shown in Figure 2. After several trials the sequence of the specimen preparation was established as follows:-

a) The extruded rods are cut to length, the off-cuts being preserved for micrographic work. About 3" length at each end of the rods is impregnated under vacuum by phenol formaldehyde and then cured at 140°C.

b) The external 1.00" and 1.10" diameters are turned down and a concentric 0.610" diameter hole bored. The external diameter of the gauge length is then carefully turned down to 0.730" diameter.

c) A fine air-escape hole is drilled 3" from the top of the bore and a close-fitting graphite plug pushed into the hole. This plug completely fills the top 2 3/4" of the bore and is bonded with phenol formaldehyde.

d) The holes for the loading pins and strain measuring arm are drilled in a positioning jig.

This type of specimen has been found satisfactory. The impregnation and the bonded plug have prevented the failures around the top loading pin which were encountered in the earlier experiments.

1.2 Heating unit

A layer of carbon felt has been sewn to the inner surface of the inner carbon radiation shield. The felt has greatly reduced the power input necessary to attain a given temperature

1.3 Load measuring unit

A fine pressure control valve before the reversing valve and a small accumulator before the actuator have been added to the hydraulic system.

The load is now automatically controlled by a signal from the digital voltmeter. A decay in load, such as that which occurs during creep, produces a change in the signal of the load transducer from a pre-determined figure. This change is caused to open the hydraulic reversing valve, which is normally closed, giving a hydraulic pulse to the actuator. The 'line' pressure is only fractionally above the actuator pressure and is applied for 1/3 second. The digital voltmeter provides a correction every 1/3 second. This maintains constancy of load to within ±1%.

1.4 Proposed modifications

A small uni-directional drift occurs in the output of the oscillator-demodulator unit, requiring manual correction several times per hour. An improved unit, with greater stability, is under construction.

It is hoped to couple an XY recorder onto the strain and load measuring units; this will improve the recording of the loading curve and so permit faster loading rates. At present the loading time is about 2 minutes to full load, if the stress-strain curve is to be plotted. This results in some creep occuring during loading.

1.5 Calibration

A rod, carrying a mirror at its exposed end (Figure 3), was coupled to the strain transducer in the normal way used for specimens. A 5m. long curved mm. scale has been permanently installed near the rig. This

scale has a radius of 8m. with the specimen axis as its centre, and is used for checking the transducer at frequent intervals.

Over a range of 20°, the output of the transducer was found to be linear, with an output of 1mV per 0.0025° of specimen rotation. (Input to the transducer was 8.000 ± 0.001 V at 1200 c/s). Using the data amplifier, a signal of 1 mV per 0.00031° of rotation was normally employed.

A mild steel specimen (Figure 4) was mounted in the apparatus in an identical manner to the graphite specimens. A plot of the load transducer reading versus the strain transducer was obtained. From a knowledge of the torsional modulus of steel, the specimen dimensions, and the strain transducer calibration, the actual values of load exerted could be calculated (Appendix 1). This method of calibration involves no assumptions regarding zero twist in the specimen holders or supports.

In all the experimental work the load was very slowly applied until a small movement occured in the strain reading. The load reading was noted and the load increased to give a known increment from that reading. This technique avoided errors due to small mechanical movements within the load unit.

1.6 Experimental procedure

The specimen was placed in position with the transducers set to have their whole linear range available. The apparatus was evacuated to 10^{-3} mm. of Hg and then the power slowly increased until the specimen reached 1500°C. It was then allowed to soak for 5 minutes at 1500°C under the full vacuum. After this, the vacuum was throttled off and argon admitted as the temperature rose. The atmospheric pressure of argon is reached at a specimen temperature of 2000°C. The argon is now supplied direct from a cylinder and no attempt is made to purify it. Previous attempts tended to introduce more impurities than they removed. During testing, the pressure is maintained at about atmospheric, with 2-5 cu. ft. per hour of argon passing through.

The rate of temperature rise was controlled, as too rapid a rise was found to cause some thermal cracking. The apparatus can achieve 2000°C in less than 1 minute when full power is applied.

The specimens were soaked for five minutes at the testing temperature and then the initial strain reading noted. After determining the load zero (see above), the load was increased in constant stress increments of about 200 p.s.i. and the immediate strain at each stress noted.

After a given creep strain had been reached, or a given time had elapsed, the actuator was reversed, thus removing the load very rapidly, the strain reading being noted at three second intervals.

At the conclusion of the recovery period, the temperature was lowered

in 100°C steps, and the change in strain observed.

2. Materials tested

These have so far been restricted to two related commercial grades, Morgan's E.Y.9 and C.Y.9. The latter, consisting principally of a mixture of ground petroleum coke, artificial graphite, and carbon black in a pitch bond, has been carbonised only. After 'graphitisation' at about 2500°C it becomes E.Y.9.

A special experimental material, made by the Morganite Carbon Co. Ltd., is now available. It consists of ground petroleum coke in a pitch binder with 10% ground artificial graphite added for ease of manufacture. The extruded rods were carbonised at 1200°C. Part of this batch has been 'graphitised at 2500°C for thirty minutes.

Consideration has been given to the procurement of pyrolytic graphite test specimens. It should be possible to make a specimen of our usual size by deposition inside a conventional graphite tube, subsequently machining it away over the gauge length. The composite tube on either side of the gauge length could easily be pinned to solid graphite rods. The cost of such specimens is not yet known.

While pyrolytic graphite would be an interesting experimental material in view of its unique properties, its use would raise problems. Prime amongst these are the internal stresses which are developed due to thermal expansion, and those due to the incompatibility of this expansion with other materials, including artificial graphite. The existence of internal stresses would make it extremely difficult to produce a uniform batch of specimens.

3. Results

These results were presented in a paper entitled 'Some Creep and Recovery Characteristics of Carbon and Graphite' by A.J. Kennedy and A. Younger at the Sixth Biennial Carbon Conference in Pittsburgh in June 1963.

3.1 Torsional stress-torsional strain curves of E.Y.9.

The curves are shown in Figure 5 and show a decreasing modulus throughout the whole temperature range from 2000 - 2850°C. This would be expected since the reported (2,3) maximum in elastic moduli occurs in the range 1600 - 2000°C. It is felt that the accuracy of these results will be improved, in future, by the use of an XY recorder.

3.2 Torsional creep of E.Y.9.

Some typical curves over ranges of temperature and stress are shown in Figures 6 and 7. At 2000°C, and under a comparatively high stress,

the creep becomes almost zero at long times. The effects of changes in stress for constant temperatures are seen for 2250°C and 2600°C in Figures 8 and 9 respectively. At 2250°C, an increase of 130% in the stress produces a 75% increase in strain after 100 minutes, whereas at 2600°C a 100% increase in stress produces a 310% increase in strain after 10 minutes. An interesting point at 2600°C is the parallel nature of the curves for the two high stress levels.

Figure 10 shows the effect of changes in testing temperature for a constant testing stress over the temperature range 2250°C to 2700°C. Increasing temperature increases the creep rate. The tests were not carried through to fracture, but were stopped at given strains.

3.3 Torsional recovery of E.Y.9.

The recovery of E.Y.9, expressed as a percentage of the total strain in the specimen at the conclusion of straining, is shown as a function of time in Figure 11. The rate of recovery appears to be very similar over the whole temperature range from 2000 - 2600°C. Trends worth noting are that (a) the proportion recoverable in a given time decreases with increasing temperature, and (b) as the initial strain increases, the proportion recoverable in a given time decreases. The rate of recovery at 2400°C does not appear to be very dependent on the initial strain (Figure 12).

Figure 13 shows the recovery at temperature after straining to a constant total strain of 3° per inch (0.191 shear strain) at temperatures in the range 2250°C to 2600°C, under a constant stress of 2000 p.s.i. All curves will, of course, eventually tail over, as does the one at 2600°C. The vertical position of the 2600°C below that for 2500°C is brought about by changes in the elastic portion of the strain which appear to occur at that temperature.

3.4 Activation energy for creep in E.Y.9.

It has been shown in metals[4] that the creep recovery can be identified as the anelastic component of the first stage of creep if the plastic deformation is small. If the recovery and the creep are plotted on the same scale (as seen in Figure 14 for E.Y.9 at 2500°C) the recovery may be subtracted from the total creep. The resultant curves show that the plastic strain component increases linearly with time. If the slope of this line, over a range of temperatures, is plotted as a function of T^{-1} (Figure 15), a straight line is obtained. By calculation, the slope of this line gives a value of 154 Kcals per mole for the activation energy for this plastic component of creep. This value is close to that reported[5] for the activation energy for self-diffusion in graphite.

3.5 Torsional stress-strain curves, creep, and recovery of C.Y.9.

Since this material has not received the 'graphitising' anneal, the

thermal history of the specimen prior to the application of the load is important. The heating cycles employed are given in Appendix 2.

The torsional stress-strain curves for three temperatures are shown in Figure 16. Those for 2250°C and 2400°C are similar to those found at these temperatures for E.Y.9, but that for 2000°C is appreciably different. Although the stress-strain curves for E.Y.9 and C.Y.9 are similar at 2250°C and 2400°C, their creep curves are very different. The creep rate of C.Y.9 is very much faster than E.Y.9 (Figure 17).

The recovery of C.Y.9 is considerably less than that found in E.Y.9 (Figure 18), but shows the same trend of decreasing recovery with increasing temperature.

3.6 Recovery on cooling.

Some evidence was obtained suggesting that lowering the temperature after a considerable recovery had occurred could increase the rate of creep recovery. This is thought to be a real effect, partly due to the thermal stresses introduced on cooling. The cooling data obtained so far are not comprehensive enough to be quantitative on this point.

3.7 Micrographic studies

An attempt was made to examine the structures of E.Y.9 and C.Y.9 before and after creep, but this structure is so complex that little change could be observed. The introduction of simpler materials, and possibly the techniques of ionic and chemical etching, should facilitate this study.

Samples cut from the C.Y.9 specimens which had been crept at graphitising temperatures were supplied to Aeon Laboratories Ltd., Beech Hill, Englefield Green, Egham, Surrey, for electron microscopic and diffraction studies. Their results will be reported under Contract No. DA-91-591-E.U.C. 1851.

B. Implications of the results

One of the original purposes of this work has now been accomplished, i.e., the study of the creep and recovery characteristics of a commercial graphite and the determination of an activation energy for creep. Nevertheless, the whole subject of the high temperature mechanisms of deformation in graphite is far from clear, and it is felt that the work can be fruitfully extended.

An activation energy for the second stage of creep, of the same order as that for self-diffusion, as occurs in metals, could imply that a metallic type of deformation occurs in this graphite. This is, however, an oversimplified picture for the following reasons.

a) The activation energy for self-diffusion is not single-valued but varies according to crystallographic direction.

b) The material studied (E.Y.9) is a complex mixture, and there is little knowledge as to which phase contributes most to the creep deformation. The material has a preferred orientation in one phase, the degree of which can vary, and this would influence the deformation mechanism. Some allowance should also be made for the porosity of the material, since the large number of pores may influence the ease of deformation.

Because of these difficulties, it would be interesting to study pyrolytic graphite, which is a single phase material, theoretically dense, and with a uniform crystallographic orientation. The inherent difficulties caused by internal stress have already been discussed. Until pyrolytic test specimens are available, we intend to investigate some simpler artefact graphites.

c) The activation energy for the second stage of creep has been calculated, assuming the equivalence of creep recovery with the anelastic first stage. Little is known about either of these process in graphite, and it would be of considerable interest to study them further to substantiate this assumption physically.

The creep of C.Y.9 is appreciably different from that of E.Y.9 and this, in part, may be due to graphitisation in the ungraphitised binder and petroleum coke. The effect of an applied stress on graphitisation might be studied by an extension of this technique.

In conclusion, therefore, this work has indicated a metallic type of secondary creep in graphite at high temperatures, but until we have investigated the actual deformation processes further, it can be regarded as no more than an indication.

Annex Personnel

The whole programme has been carried out by a graduate scientist (Dr. A. Younger) and a laboratory technician (Mr. R.C. Walding) under the general direction of Professor A.J. Kennedy. Dr. Younger and Mr. Walding have been employed full time on this project throughout the year. In addition, about 1000 man hours have been contributed by Departmental workshop personnel.

Dr. Younger attended the Sixth Biennial Carbon Conference held in Pittsburgh in June, 1963, and presented a paper on this work. He also visited a large number of laboratories working on graphite in the U.S.A. His itinerary is appended (Appendix 3).

No capital equipment of any great value was purchased in the period of this report, the major expenditure having occurred the previous year. Expenditure on materials was approximately as follows.

a)	Test materials	£50 + a considerable quantity supplied free of charge by Morganite Carbon Co. Ltd.
b)	Element material, plus machining costs	£30
c)	Argon	£70
d)	Carbon felt	£10
e)	Phenol formaldehyde	£5
f)	Maintenance of the electronics equipment	£40
g)	Electronic replacements	£20
h)	Nimonic alloy (for specimen pins)	£15
	plus small quantities of hydraulic and vacuum oils, greases, seals, etc., and general stores items.	

References

1. F.T.R. No. 1. Contract DA-91-591-E.U.C. 1759.

2. J.F. Andrew and D.C. Wobschall, Proc. 5th Carbon Conference, 1961, Vol. 2.

3. H.W. Davidson, H.H.W. Losty and A.M. Ross, Industrial Carbon and Graphite, Soc. of Chem. Ind., London, 1958.

4. A.J. Kennedy, Nature, 195, 898-899 (1962).

5. M.A. Kanter, Phys. Rev., 98, 1563 (1955).

Appendix 1

Calculations involved in the load calibration

For any shaft, the angle of twist, is given by

$$\theta = \frac{T\ell}{NJ}$$

where T is the applied torque
ℓ the length of shaft
J its polar moment of inertia
N the modulus of the shaft material.

For a tube

$$J = \frac{\pi}{32} (D^4 - d^4)$$

where D and d are the external and internal diameters respectively.

For this steel specimen

$$\theta = \frac{T}{N} \left(\frac{\ell_1}{J_1} + \frac{\ell_2}{J_2} + \frac{\ell_3}{J_3} \right)$$

where ℓ_1 is the distance between the centre line of the upper pin and the gauge length,
ℓ_2 is the gauge length, and
ℓ_3 is the distance between the gauge length and the centre line of the strain transducer arm.
J_1, J_2 and J_3 are the respective polar moments of inertia.

Substituting actual values, we have

$$\theta = \frac{32T}{\pi N} \left(\frac{2.25}{0.687} + \frac{3.00}{0.0608} + \frac{8.562}{1} \right)$$

and hence

$$\theta = \frac{626T}{N}$$

If N for mild steel is taken as 11.54×10^6 p.s.i.

then

$$\theta_{rad} = \frac{626 \times T}{11.54 \times 10^6}$$ where T is in lb. - in.

or

$$T = \frac{\theta^\circ}{3.1} \times 10^3$$

But from the strain transducer calibration, a specimen twist of 1° would produce a voltage change on the strain transducer by means of the relationship

$$T = \frac{10^3}{3.1 \times 0.406} \quad \Delta V \text{ lb. - in.}$$

where ΔV is the voltage change at the set conditions.

Hence

$$T = 7.95 \times 10^2 \, \Delta V \text{ lb. - in.}$$

Appendix 2

Heating cycles employed on C.Y.9 specimens

Heating to 2000°C

$1\frac{1}{2}$ hours soak at 1500°C.
Almost instantaneous rise to 1750°C.
5 mins. at 1750°C.
Almost instantaneous rise to 2000°C.
Soak 5 mins. at 2000°C, then test.

Heating to 2250°C

Heat to 1500°C.
Slow heating over 10 mins. from 1500 to 1900°C.
Rapid rise to 2000°C.
Slow heating over 10 minutes from 2000 to 2250°C.
Soak 5 minutes at 2250°C, then test.

Heating to 2400°C

Heat in 5 mins. to 1500°C.
Rapidly heat to 1750°C and soak for 5 mins.
Rapidly heat to 1900°C and soak for 5 mins.
Rapidly heat to 2150°C and soak for 5 mins.
Rapidly heat to 2250°C and soak for 5 mins.
Rapidly heat to 2400°C and soak for 5 mins., then test.

Itinerary

Appendix 3

DATE 1963	PLACE	HOST
14th June	Departure by M.A.T.S. from Mildenhall.	
15th June	Arrival McGuire A.F.B.N.J. and travel by road to Pittsburgh.	
17th-21st June	Attendance at 6th Carbon Conference, Pittsburgh.	
20th June afternoon	Research Laboratory, Allegheny-Ludlum Steel Co.	Dr. L.S. Ames
21st June	Travel Pittsburgh to San Francisco.	
24th June	Visit Lockheed Missile and Space Co. Ltd., Palo Alto, California.	Dr. R.H. Bragg
24th June evening	Travel to Pasadena via Los Angeles.	
25th June	Jet Propulsion Laboratory Pasadena, California.	Dr. W.V. Kotlensky
26th June	Aeronutronics Division of Ford Motor Co. Newport Beach, California.	Dr. R.M. Hale
27th June	Travel from Los Angeles to Cleveland, Ohio.	
28th June	Parma Research Lab., National Carbon Co., Cleveland.	Dr. E.J. Seldin
28th June evening	Travel to Buffalo by road.	
29th June	Discussion with Dr. W.E. Parker of Speer Carbon Co.	
1st July	Carbon Research Laboratory, State University of New York, Buffalo.	Professor S. Mrozowski
1st July evening	Travel to Schenectady by road	
2nd July	Research Laboratory, General Electric Co.	Dr. E.R. Stower and Dr. R.H. Diefendorf
2nd July evening	Travel to Boston	
3rd July morning	U.S. Army Materials Research Agency, Watertown Arsenal, Boston.	Dr. A.P. Levitt and Mr. A. Tarpinian

3rd July afternoon	High Temperature Materials Inc., Boston.	Dr. D. Schiff
5th July	Travel to New York by road	
6th July	Travel to McGuire by road	
6th July	Departure by M.A.T.S. from McGuire	
7th July	Arrival Mildenhall.	

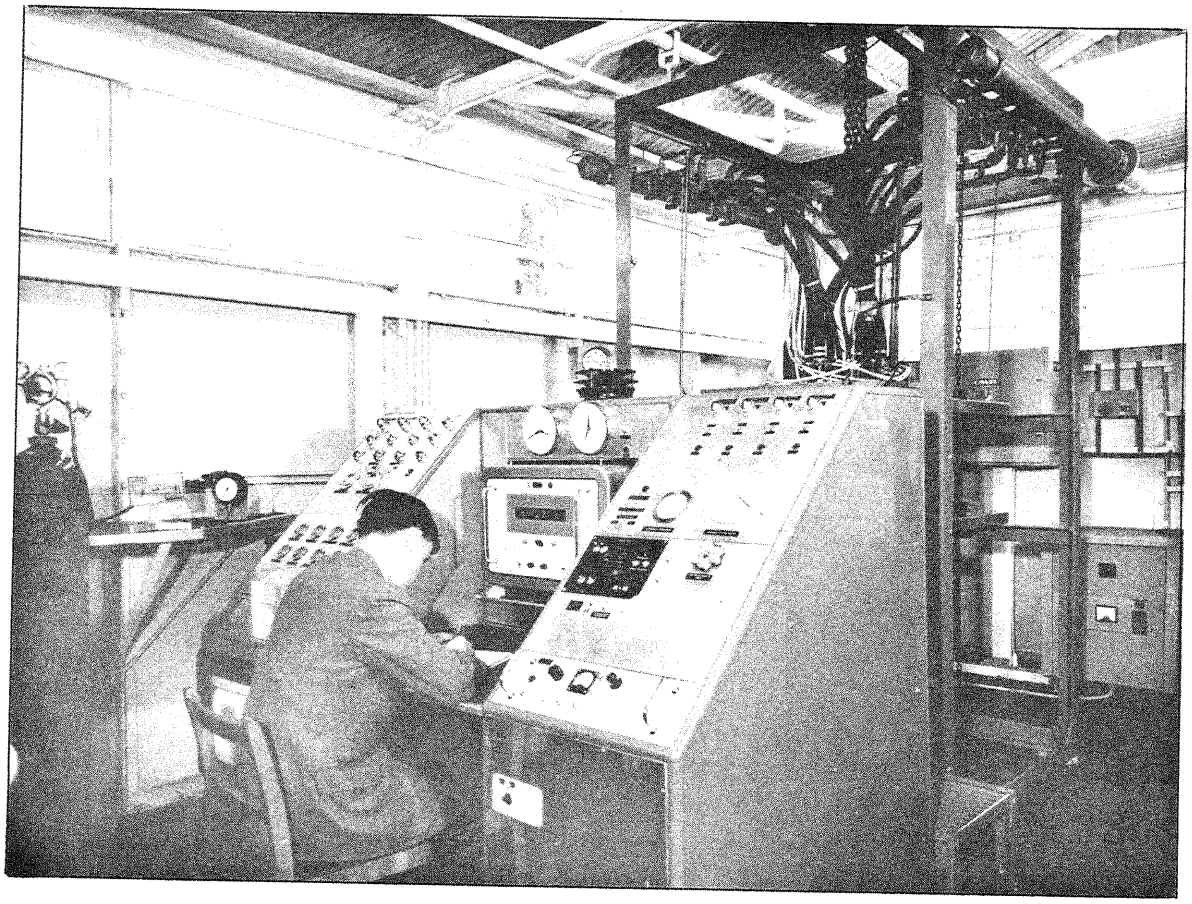


FIG. 1 A GENERAL VIEW OF THE APPARATUS.

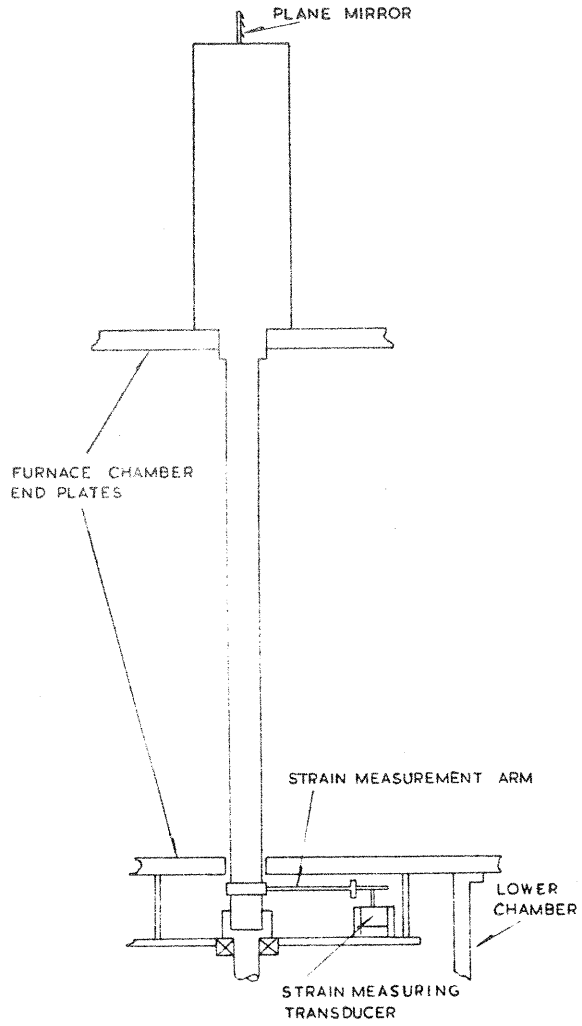
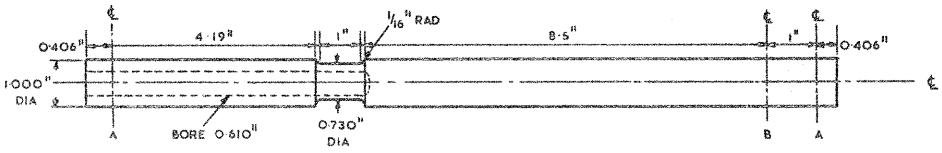


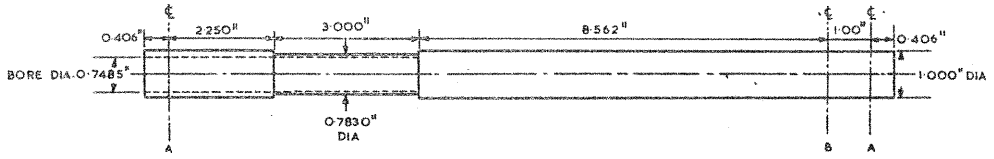
FIG. 3 DRAWING OF STRAIN CALIBRATION ARRANGEMENT.



A – 0·250" HOLE FOR LOADING PINS

B – 0·125" HOLE FOR STRAIN TRANSDUCER ARM.

FIG. 2 DIMENSIONED DRAWING OF TEST SPECIMEN.



A = CENTRE – LINE OF HOLES 0·250" DIA FOR LOADING PINS.

B = CENTRE – LINE OF HOLE 0·125" DIA FOR STRAIN-TRANSDUCER ARM.

FIG. 4 DIMENSIONED DRAWING OF MILD STEEL SPECIMEN.

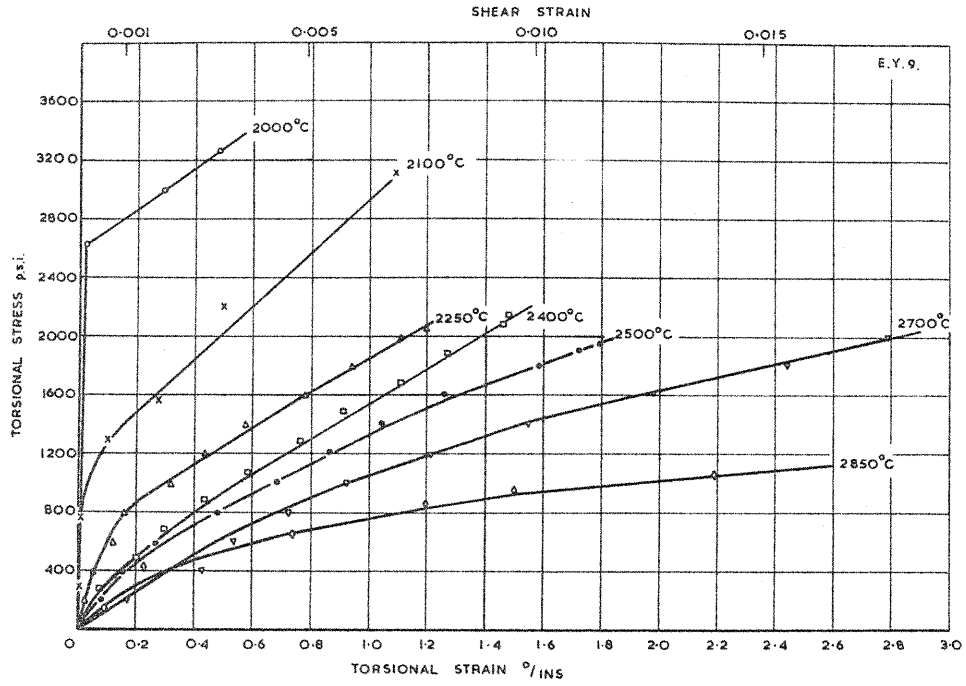


FIG. 5 TORSIONAL STRESS-TORSIONAL STRAIN CURVES OF E. Y. 9 OVER A RANGE OF TEMPERATURES.

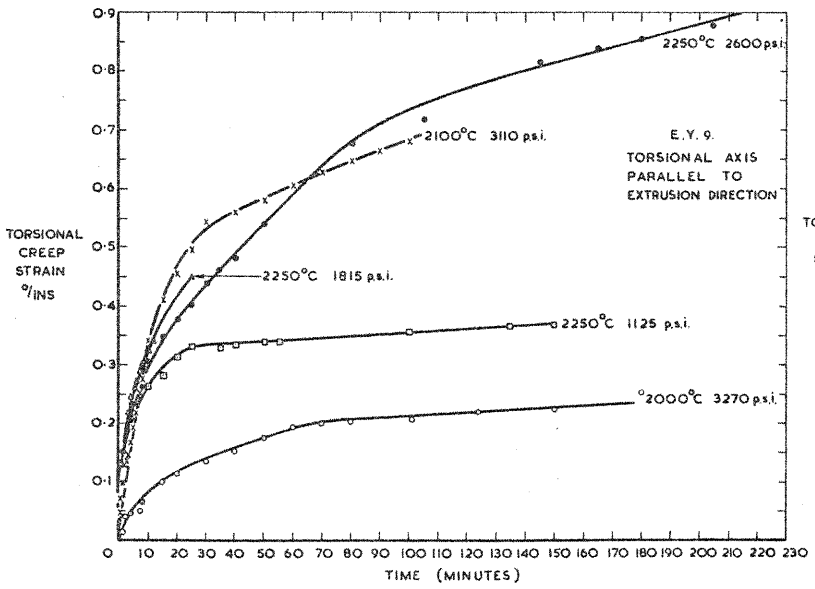


FIG. 6 TORSIONAL CREEP CURVES OF E. Y. 9 OVER A RANGE OF TEMPERATURES.

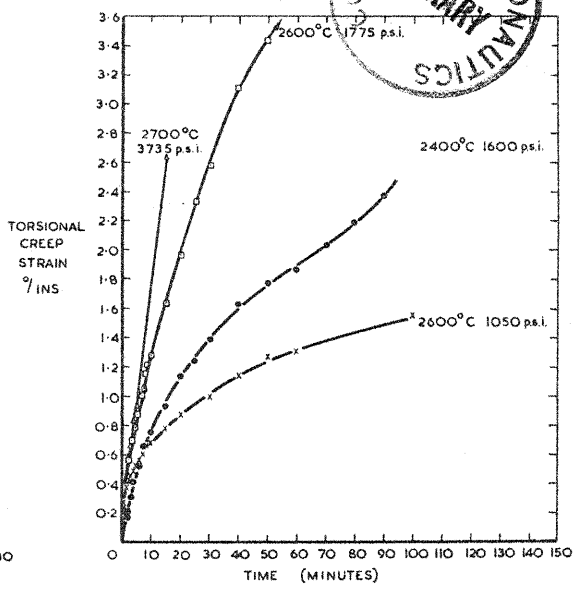


FIG. 7 TORSIONAL CREEP CURVES OF E. Y. 9 OVER A RANGE OF TEMPERATURES.

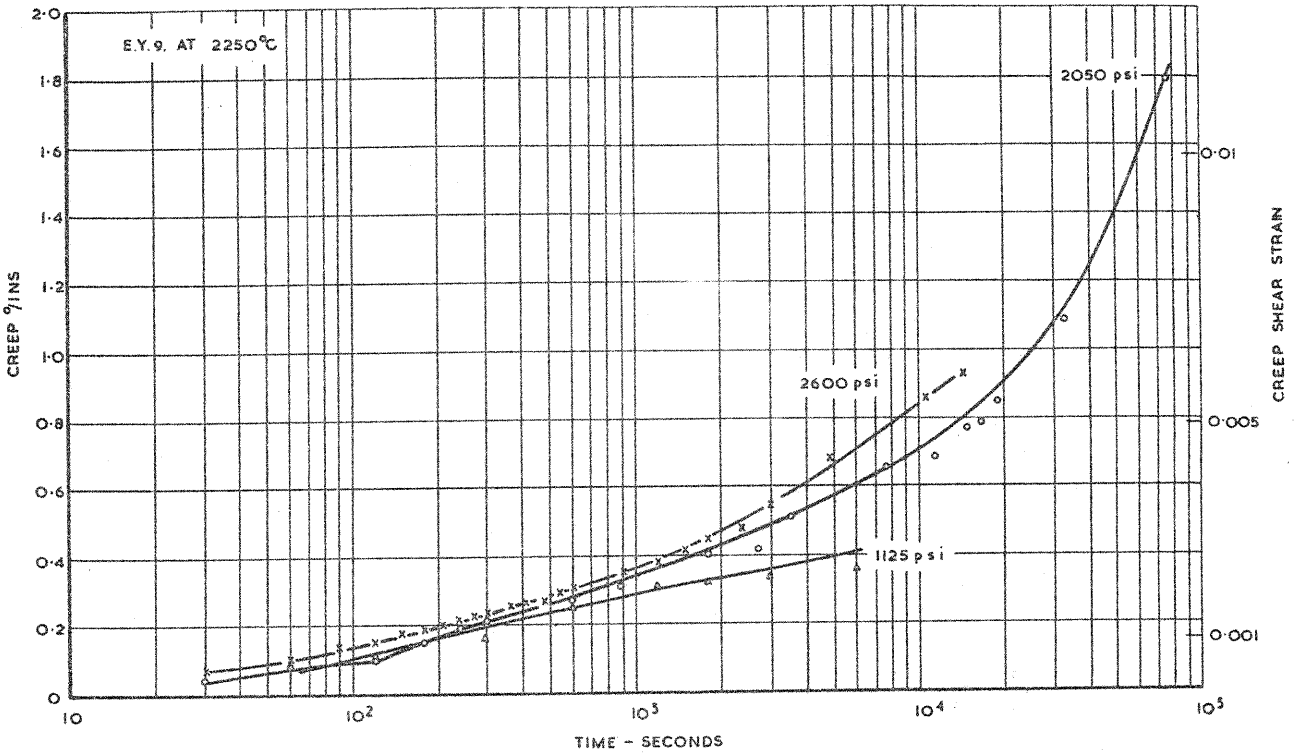


FIG. 8 TORSIONAL CREEP OF E.Y.9 AT 2250°C.

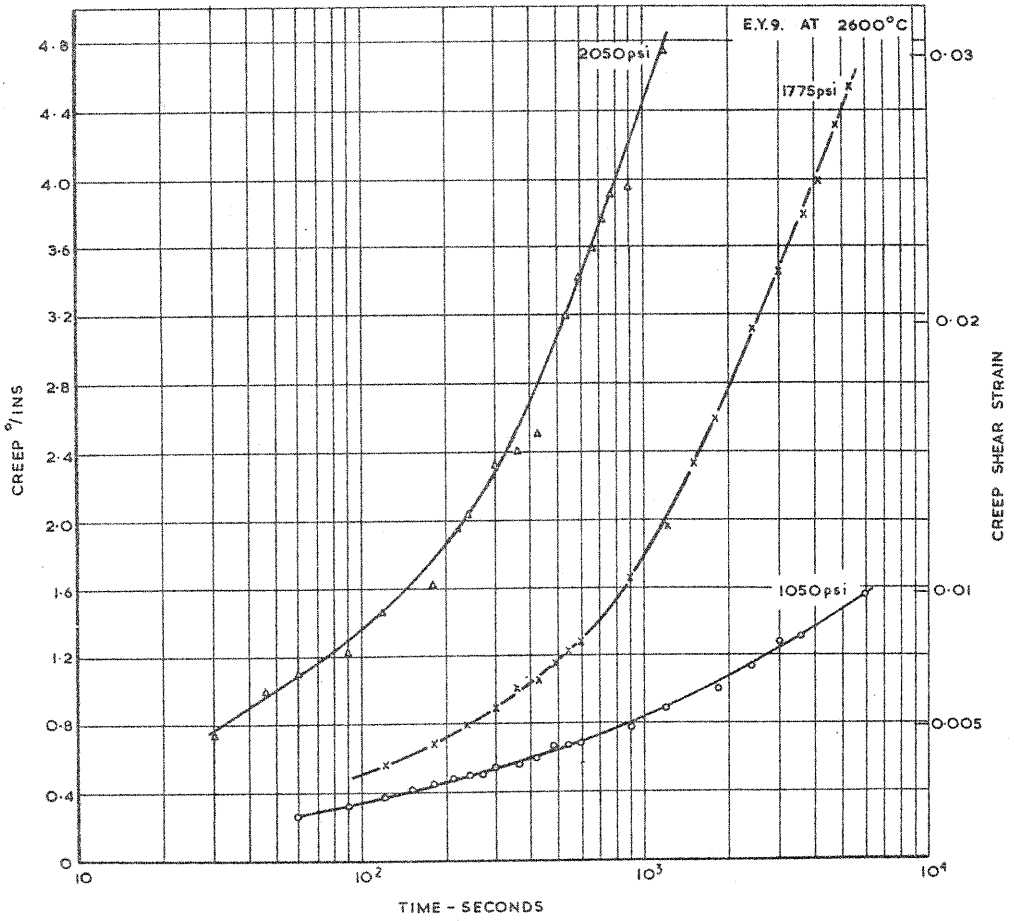


FIG. 9 TORSIONAL CREEP OF E.Y.9 AT 2600°C.

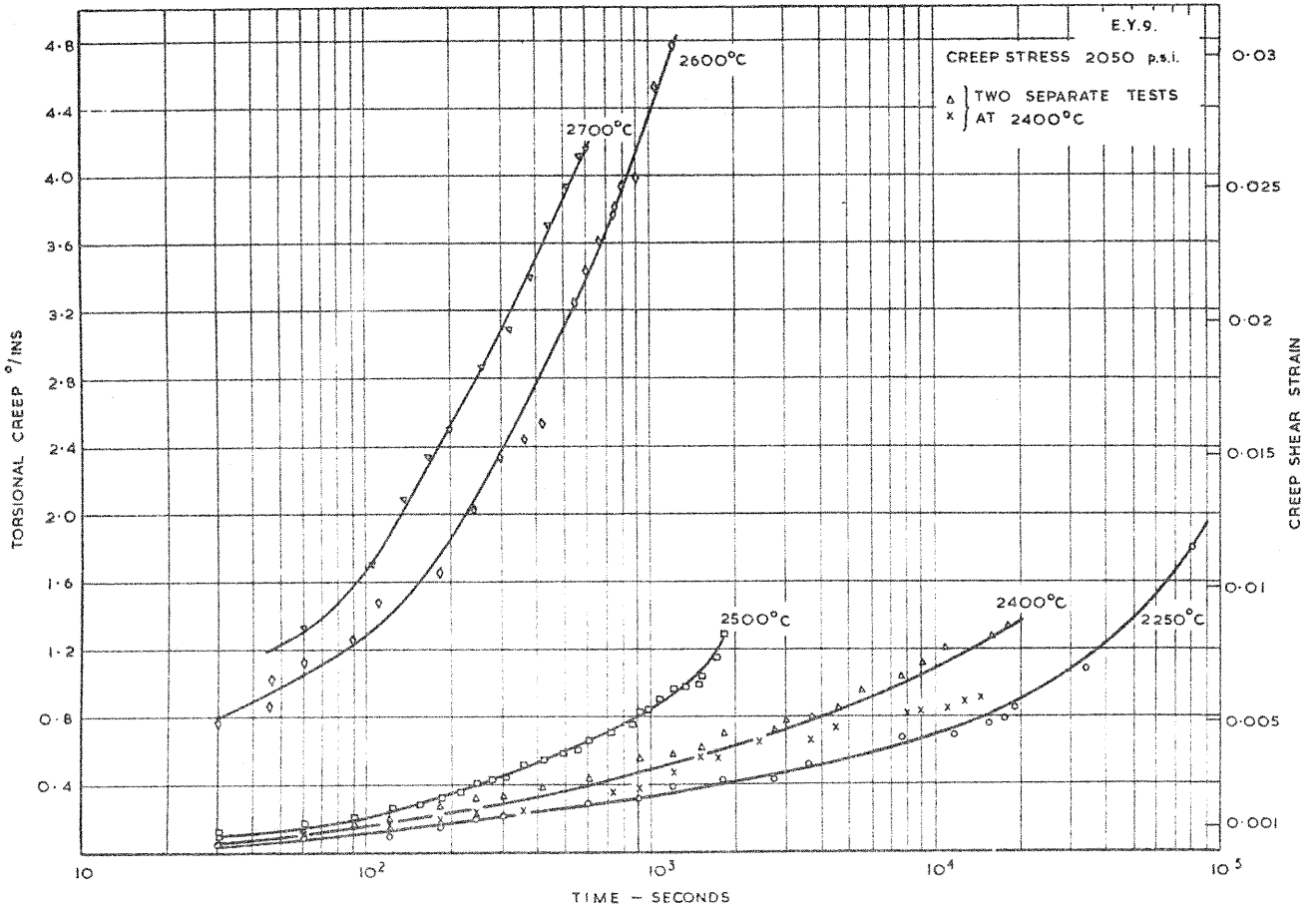


FIG. 10 TORSIONAL CREEP OF E.Y.9 UNDER 2000 P.S.I. STRESS AT A RANGE OF TEMPERATURES.

E.Y.9 RECOVERY

SYMBOL	TEMP°C	INITIAL STRAIN °/INS
○	2000	0·739
×	2250	1·767
⊕	2400	3·813
▲	2400	5·41
⊡	2600	2·50
▼	2600	6·07

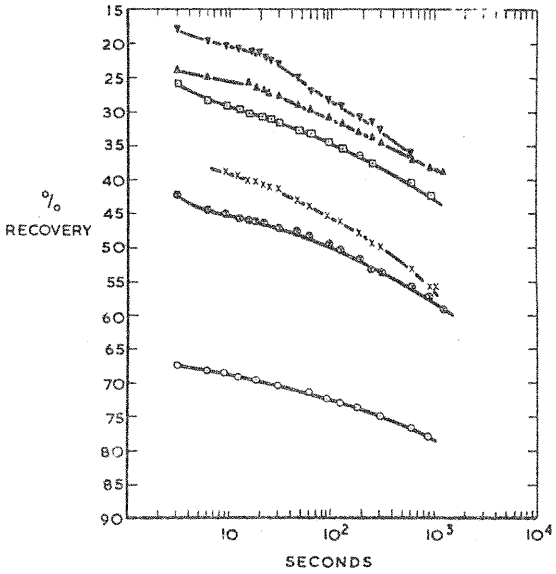


FIG. 11 TORSIONAL RECOVERY OF E.Y.9 OVER A RANGE OF TEMPERATURES.

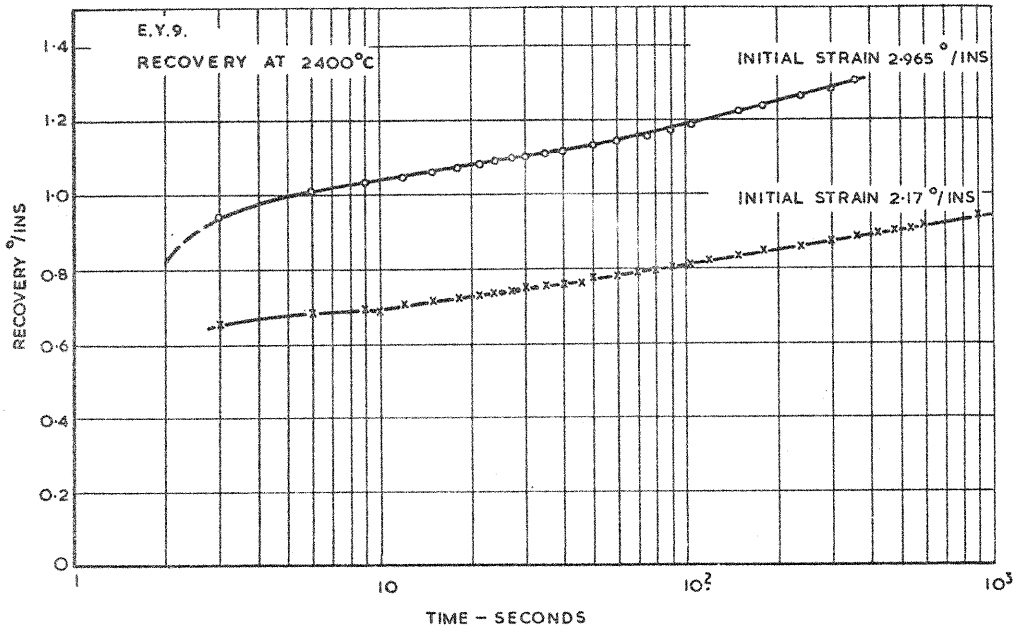


FIG. 12 TORSIONAL RECOVERY OF E.Y.9 at 2400°C AFTER DIFFERENT STRAINS.

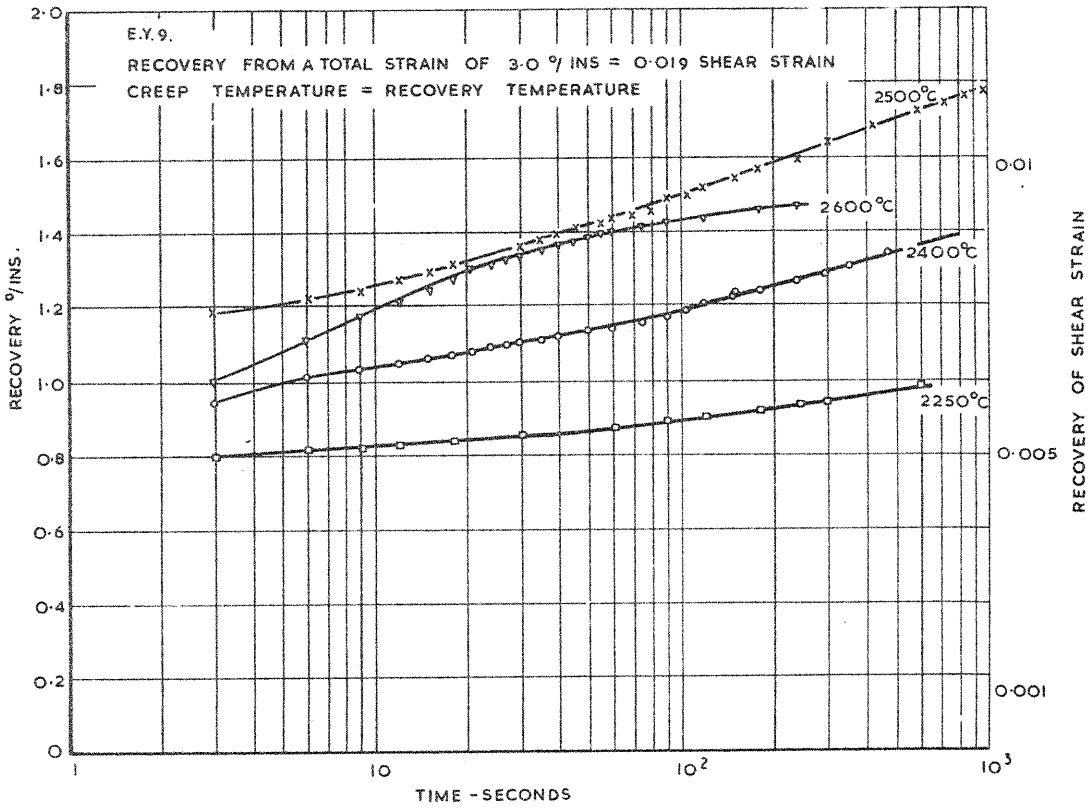


FIG. 13 TORSIONAL RECOVERY AFTER CONSTANT STRAIN OVER A RANGE OF TEMPERATURES

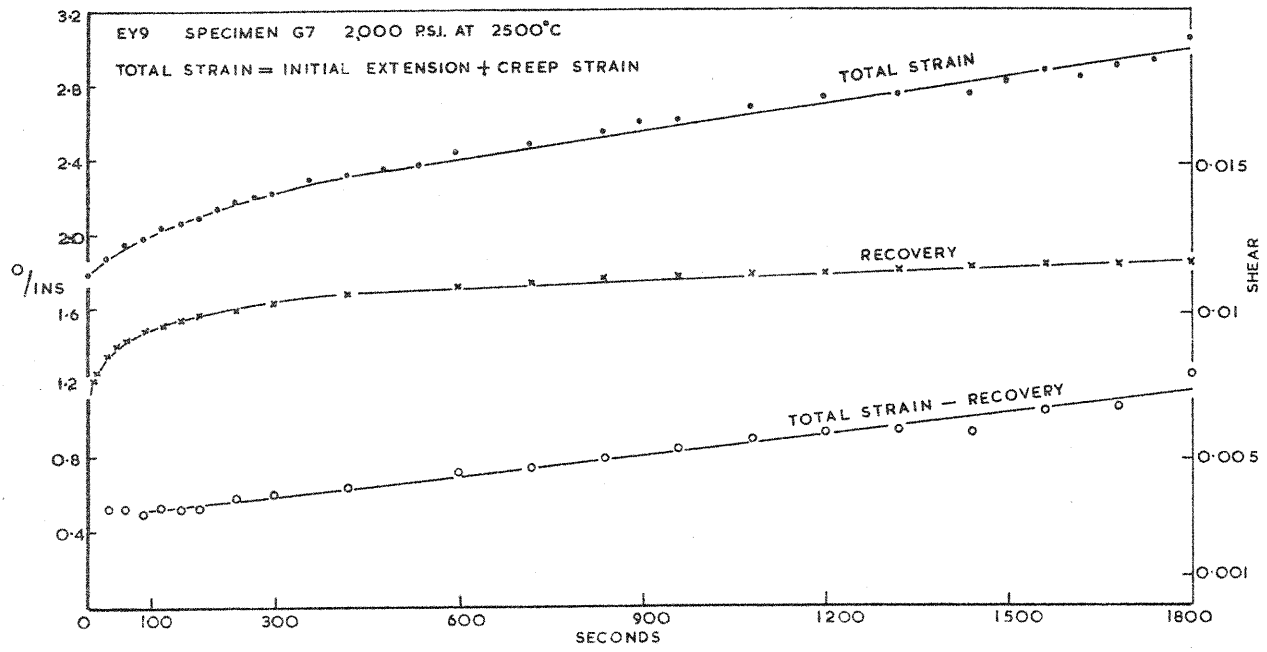


FIG. 14 CREEP, RECOVERY, AND RESULTANT PLASTIC STRAIN IN E.Y.9 AT 2500°C.

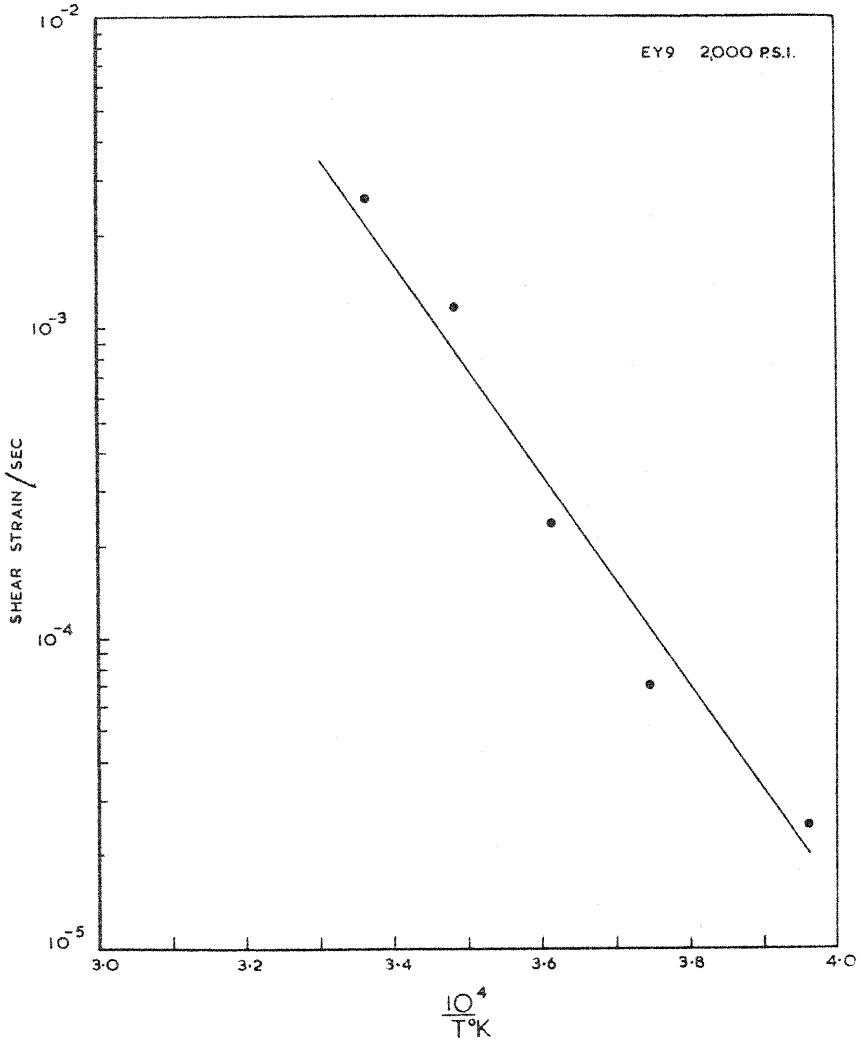


FIG. 15 RATE OF PLASTIC COMPONENT VS. RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

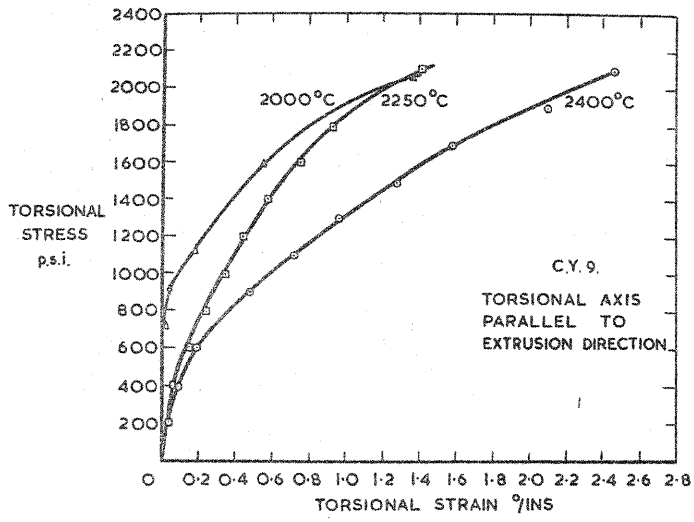


FIG. 16 TORSIONAL STRESS-TORSIONAL STRAIN CURVES OF C.Y.9 AT THREE TEMPERATURES.

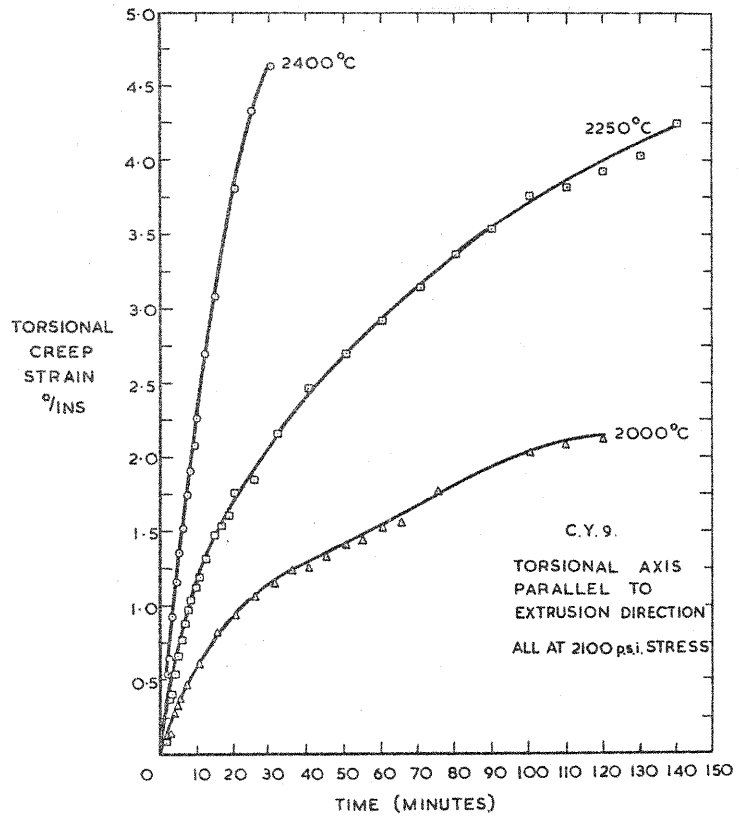


FIG. 17 TORSIONAL CREEP CURVES UNDER 2000 P.S.I. STRESS FOR C.Y.9 AT THREE TEMPERATURES.

C.Y.9 RECOVERY

SYMBOL	TEMP°C	INITIAL STRAIN °/INS
△	2000	3·46
⊡	2250	5·8
⊙	2400	7·08

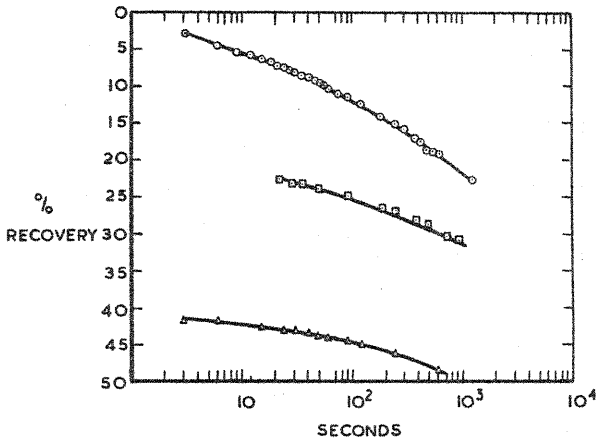


FIG. 18 TORSIONAL RECOVERY FOR C.Y.9 AT THREE TEMPERATURES.